

A  
wrong sequence  
of  
layers

DERWENT-ACC-NO: 1999-584178

DERWENT-WEEK: 200003

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TITLE: Catalyst for purifying exhaust gas containing NOx  
ejected from internal combustion engine, motor vehicles -  
consists of platinum, palladium, rhodium and layer  
containing silica

PATENT-ASSIGNEE: NISSAN MOTOR CO LTD[NSMO]

PRIORITY-DATA: 1998JP-0058375 (March 10, 1998)

PATENT-FAMILY:

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APPLICATION-DATA:

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INT-CL (IPC): B01D053/94, B01J023/58

ABSTRACTED-PUB-NO: JP 11253758A

BASIC-ABSTRACT:

NOVELTY - The catalyst consists of platinum, palladium, rhodium and first layer containing alkali, alkaline earth and rare earth elements. The second layer consists of beta zeolite and silica with third layer containing zeolite having copper and/or cobalt. DETAILED DESCRIPTION - An INDEPENDENT CLAIM is also included for the exhaust gas purification method.

USE - For purifying exhaust gas containing NOx ejected from internal combustion engine, combustor automobile engine etc.

ADVANTAGE - Even exhaust gases with low hydrocarbon and low NOx content is purified efficiently, thus leading to less environmental pollution. Motor vehicles with excellent fuel efficiency is provided.

CHOSEN-DRAWING: Dwg. 1/3

TITLE-TERMS: CATALYST PURIFICATION EXHAUST GAS CONTAIN EJECT INTERNAL COMBUST  
ENGINE MOTOR VEHICLE CONSIST PLATINUM PALLADIUM RHODIUM LAYER  
CONTAIN SILICA

DERWENT-CLASS: E36 H06 J04

CPI-CODES: E11-Q02; E31-H01; E31-P03; E35; H06-C03B; J04-E04; N01-D02;  
N02-E02; N02-F02; N06-A; N06-B01;

CHEMICAL-CODES:

Chemical Indexing M3 \*01\*

Fragmentation Code

A100 A119 A155 A200 A212 A220 A256 A545 A546 A657  
A678 A700 A758 C810 M411 M730 M903 Q421

Chemical Indexing M3 \*02\*

Fragmentation Code

A313 A427 A429 A940 B114 B701 B702 B712 B720 B831  
C108 M411 M730 M903 Q421

Chemical Indexing M3 \*03\*

Fragmentation Code

C107 C108 C307 C520 C730 C800 C801 C802 C803 C804  
C807 M411 M750 M903 M904 M910 N163 N441 Q431 Q436  
Q439

Specific Compounds

01784K 01784X

Registry Numbers

1784U

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(54)【発明の名称】 排気ガス浄化用触媒及び排気ガス浄化方法

(57)【要約】

【課題】 150℃以下の低温を含む条件で、しかも低いHC/NO<sub>x</sub>比条件の排気ガスが高効率で浄化可能な排気ガス浄化用触媒及び排気ガス浄化方法を提供すること。

【解決手段】 白金(Pt)成分、パラジウム(Pd)成分及びロジウム(Rh)成分から選ばれた1種以上の成分と、アルカリ成分、アルカリ土類成分及び希土類成分から選ばれた1種以上の成分を含む触媒層を第1触媒層とし、その上にβゼオライトを含む第2触媒層を設け、さらにその上に銅(Cu)成分及び/またはコバルト(Co)成分を含有するゼオライトを主成分とする第3触媒層を設けた排気ガス浄化用触媒において、第2触媒層にシリカ(SiO<sub>2</sub>)を含有させる構成とした。

## 【特許請求の範囲】

【請求項1】 白金(Pt)成分、パラジウム(Pd)成分及びロジウム(Rh)成分から選ばれた1種以上の成分と、アルカリ成分、アルカリ土類成分及び希土類成分から選ばれた1種以上の成分を含む触媒層を第1触媒層とし、その上にβゼオライトを含む第2触媒層を設け、さらにその上に銅(Cu)成分及び／またはコバルト(Co)成分を含有するゼオライトを主成分とする第3触媒層を設けた排気ガス浄化用触媒において、第2触媒層にシリカ(SiO<sub>2</sub>)を含有させることを特徴とする排気ガス浄化用触媒。

【請求項2】 請求項1記載の排気ガス浄化用触媒において、第2触媒層の直径1nm以上4nm以下の細孔の容積和が、直径1nm以上100nm以下の細孔の容積総和の50%以上であることを特徴とする排気ガス浄化用触媒。

【請求項3】 請求項1または2記載の排気ガス浄化用触媒において、第2触媒層に含有するシリカ量がβゼオライトに対して10～50重量部であることを特徴とする排気ガス浄化用触媒。

【請求項4】 請求項1乃至3のいずれかの項に記載の排気ガス浄化用触媒において、第2触媒層のシリカが、粒径1nm以上4nm以下であるシリカゾルを原料とすることを特徴とする排気ガス浄化用触媒。

【請求項5】 請求項1乃至4のいずれかの項に記載の排気ガス浄化用触媒において、第1触媒層が含有するアルカリ、アルカリ土類及び希土類成分が、マグネシウム(Mg)、カルシウム(Ca)、カリウム(K)、バリウム(Ba)、ランタン(La)、ストロンチウム(Sr)、セシウム(Cs)、セリウム(Ce)から選ばれた1種以上の成分であることを特徴とする排気ガス浄化用触媒。

【請求項6】 請求項1乃至5のいずれかの項に記載の排気ガス浄化用触媒において、第1触媒層が含有するアルカリ、アルカリ土類及び希土類成分から選ばれた1種以上の成分の含有量が、ハニカム状モノリス触媒1L当たり0.1モルを超えて0.6モル以下の範囲で含有することを特徴とする排気ガス浄化用触媒。

【請求項7】 請求項1乃至6のいずれかの項に記載の排気ガス浄化用触媒を用いた排気ガス浄化方法であって、空燃比(Air/Fuel比=A/F)が14.7以上のリーン条件で運転される内燃機関の排気系に前記排気ガス浄化用触媒を設置し、酸素濃度が5%以上で、かつ窒素酸化物と炭化水素が反応して窒素酸化物を窒素に転化するのに必要な炭化水素量と窒素酸化物量の比率(以下、HC/NO<sub>x</sub>比と略記)が0を超えて10以下の排気ガスを流通、接触させることを特徴とする排気ガス浄化方法。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、内燃機関、燃焼器等から排出される排気ガスを浄化するための技術に係り、特に酸素を過剰に含むリーン排気ガス中の窒素酸化物(NO<sub>x</sub>)を高効率で浄化するのに好適な排気ガス浄化用触媒及び排気ガス浄化方法に関する。

【0002】

【従来の技術】従来の自動車エンジンの排気ガスのように酸化成分と還元成分とをはば等しく含む排気ガスを浄化するための触媒としては、3元触媒が広く用いられている。これは、Pt、Pd、Rh等の貴金属成分及びセリア(Ce)成分をはじめとする各種成分を担持した活性アルミナを主成分とする触媒であり、排気ガス中の有害成分である炭化水素(HC)、一酸化炭素(CO)及び窒素酸化物を高効率で浄化できる。

【0003】一方、近年は燃費向上、二酸化炭素の排出量削減の観点から、理論空燃比より高い空燃比でも運転するリーン・バーンエンジンが注目されている。このようなエンジンの排気ガス(リーン排気ガスという)は、理論空燃比近傍で運転する従来エンジンの排気ガス(ストイキ排気ガスという)に比較して、酸素含有率が高く、上記3元触媒では窒素酸化物の浄化が不十分となる。そこで、リーン・バーンエンジン排気ガスの窒素酸化物を高効率で浄化できる新触媒が望まれていた。

【0004】各種の金属成分をY型、L型、モルデナイト、MFIゼオライト等のゼオライトに担持したゼオライト系触媒は、リーン排気ガス中において炭化水素類の共存下でNO<sub>x</sub>を比較的効率良く浄化できる能力を有している。この金属成分としては、銅(Cu)、コバルト(Co)、銀(Ag)、ニッケル(Ni)、鉄(Fe)等の遷移金属成分、貴金属成分では白金(Pt)も有効であることが認められているが、中でもCuを担持したCu-ゼオライト系触媒が、高流速ガス条件下でも比較的優れたNO<sub>x</sub>浄化能力を示すため、自動車のような小型移動発生源や定置型の自家発電用エンジン等の排気ガス浄化への適用に期待が掛けられていた。

【0005】しかし、上記金属成分を担持したゼオライト系触媒には次の問題点があるため、リーン条件で運転される自動車の排気ガス浄化用触媒としては実用化に至っていない。まず、NO<sub>x</sub>を比較的効率良く浄化できる温度範囲が狭く、特に150℃から300℃の比較的低い温度領域では十分なNO<sub>x</sub>浄化能力が得られない。また、排気ガス中に炭化水素が比較的少ない、特にHC/NO<sub>x</sub>比が5～6以下となる条件ではNO<sub>x</sub>浄化能力が急激に低下する。さらには、水蒸気を含む高温(600℃以上)の条件(水熱条件)下で極めて劣化が激しいという根本的な問題点があるため、リーン・バーン自動車からの排気ガス浄化用触媒としては実用化に至っていない。

【0006】上記低温度領域でのNO<sub>x</sub>浄化能力の向上に対しては、例えば、Cu-ゼオライト系触媒層の下層

に貴金属触媒層を設けることにより、貴金属触媒層での反応熱を利用し、より低温から上層のCu-ゼオライト系触媒を作動させることが既に特開平1-127044号公報、特開平5-68888号公報などで提案されている。しかし、この場合は下層の貴金属触媒層における酸化反応熱のために、劣化が激しくなったり、さらには、貴金属触媒層の強い酸化活性のためにHC類が優先的に酸化消費されるので、NO<sub>x</sub>浄化率の低下を招く。この影響は、Cu-ゼオライト系触媒層に貴金属成分を共存させる場合（特開平1-31074号公報、特開平5-168939号公報）には特に大きい。

【0007】また、Pt系触媒を用いれば、200～250℃の比較的低温域でもNO<sub>x</sub>を転化できるが、N<sub>2</sub>への転化のみでなく、N<sub>2</sub>Oの生成も無視できず、環境への悪影響から、そのままでは使用できない状況にある。

【0008】Cu-ゼオライト系触媒、Pt系触媒、いずれの触媒でも、低HC/NO<sub>x</sub>比の排気ガス条件では、NO<sub>x</sub>浄化能力が不十分となる。そこで、還元剤となるHC類、アルコール類等を触媒入り口に2次的に供給する浄化方法も提案されている。この場合、還元剤のタンクを車載する方法、燃料を還元剤に直接利用する方法等が提案されているが、前者の場合にはタンクの搭載場所や重量増の問題点、後者の場合にはエンジンの燃費が犠牲になるという問題点が生ずる。

【0009】

【発明が解決しようとする課題】本発明は、低温域及び低HC/NO<sub>x</sub>比ではゼオライト系触媒のNO<sub>x</sub>浄化能力が不十分であり、かつ高温水熱条件下では劣化が激しいという上記問題点を解決し、性能を大幅に向上させた実用レベルの排気ガス浄化用触媒及び排気ガス浄化方法を提供することを目的とする。

【0010】

【課題を解決するための手段】本発明は、Pt成分、Pd成分及びRh成分から選ばれた1種以上の成分と、アルカリ成分、アルカリ土類成分及び希土類成分から選ばれた1種以上の成分を含む触媒層を第1触媒層とし、その上にシリカ及びβゼオライトを含む第2触媒層を設け、さらにその上にCu成分及び/またはCo成分を含むゼオライトを主成分とする第3触媒層を設けた排気ガス浄化用触媒を用意し、該排気ガス浄化用触媒をA/F比が14.7以上のリーンの条件で運転される内燃機関の排気系に設置し、酸素濃度5%以上、かつHC/NO<sub>x</sub>比が0を超えて10以下の排気ガスを流通、接触させることにより上記目的を達成するものであり、特に、第2触媒層にシリカ及びβゼオライトを含有させることにより、より高い浄化性能を達成するものである。

【0011】本発明になる触媒は、上記3層から成り、かつその組合せ方に大きな特徴を有している。第1触媒層はNO<sub>x</sub>を酸化してより反応性の高いNO<sub>x</sub>種に転換

する役割を有し、第3層のNO<sub>x</sub>還元剤（還元触媒）の低温活性を促進させる。第2触媒層は、排気ガスが低温域にある時にHC類を効率よくトラップし、第3層のNO<sub>x</sub>還元材が作動する温度域になるとHC類を供給してNO<sub>x</sub>の還元を促進する。ここで、第2触媒層に特定のシリカ及びβゼオライトを含有させることによりHCのトラップに好都合な細孔分布を形成し、浄化効率を著しく向上している。第1及び第2触媒層は高温水熱条件下に長時間曝されることにより劣化した第3触媒層のNO<sub>x</sub>酸化能力及びHC吸着を補い、これにより触媒の劣化分を補うのである。

【0012】上記3層の組合せ方は、NO<sub>x</sub>還元材を含む触媒層を最表面に、貴金属成分を含む触媒層を最下層に配置する。NO<sub>x</sub>還元材層と貴金属触媒層を直接接触させると活性成分同士の反応が起こるなど、触媒劣化の面で必ずしも好ましくない場合がある。本発明では、NO<sub>x</sub>還元材層と貴金属触媒層の間にシリカ及びβゼオライトを配することによりHC類の吸着特性を著しく向上させ、これにより優れた高い耐久性も実現している。

【0013】本発明では、第2触媒層における細孔分布が重要であり、それには含有させるシリカ量及びそのシリカ原料の平均粒径の影響が大きい。第2触媒層における細孔分布としては、直径1nm以上4nm以下の細孔の容積和が、直径1nm以上100nm以下の細孔の容積総和の50%以上である場合に、NO<sub>x</sub>浄化性能の向上効果が大きい。含有させるシリカ量はβゼオライトに対して10～50重量部が好ましく、そのシリカ原料の平均粒径は、1nm以上4nm以下であることが好ましい。ここで、第1触媒層が含有するアルカリ、アルカリ土類及び希土類成分としてはMg、Ca、K、Ba、La、Sr、Cs、Ceから選ばれた1種以上の成分が有効であり、該成分の含有量はハニカム状モノリス触媒1L当たり0.1モルを超えて0.6モル以下の範囲で効果が発揮される。該成分の含有量は、少ないと効果が小さく、多すぎると貴金属の効果が打ち消されてしまう。

【0014】本発明で用いる第2触媒層のβゼオライトのシリカ/アルミナ比は20以上150以下であることが好ましい。シリカ/アルミナ比が小さすぎるとゼオライト骨格が不安定になり、逆にシリカ/アルミナ比が大きすぎるとHC類を保持する力が弱くなり、第3触媒層が作動開始する温度までHC類を蓄えることが出来なくなる。また、第2触媒層のβゼオライト量としては、ハニカム状モノリス触媒1L当たり20g以上100g以下が有効である。

【0015】NO<sub>x</sub>還元材を含む第3触媒層のゼオライトとしては、Y型ゼオライト、フェリライト、モルデナイト等も活性を有するが、とりわけMFIゼオライト及び/またはβゼオライトが有効であり、そのシリカ/アルミナ比は20以上80以下が好ましい。シリカ/アルミナ比が小さすぎるとゼオライト骨格が不安定になる

と同時にイオン交換で担持される活性成分(Cu及び/またはCo)の量が過剰となり、分散性が低下して活性点1点当たりの活性が急激に低下するとともに、活性点同士の凝集が起こりやすく、いわゆるシンタリングによる劣化が進みやすくなる。しかし、シリカ/アルミナ比が大きすぎると活性点の数が少なすぎて十分な活性が得られない。

【0016】また、第3触媒層のコート(担持)量はハニカム状モノリス触媒1L当たり120g以上300g以下が好ましい。触媒層のコート量が少ないと高SV下での活性が不十分となり、逆に多すぎると、第1層、第2層への反応分子の拡散を妨げたり、圧力損失が大きくなるなどの悪影響が生じる。本発明におけるゼオライトは、水熱処理、再合成などによって、結晶性を高めるとより安定化し、耐熱性、耐久性の高い触媒が得られるので好ましい。

【0017】本発明になる排気ガス浄化用触媒を得るに当たって、ゼオライトに担持する金属成分の原料としては、無機酸塩、酸化物、有機酸塩、塩化物、炭酸塩、ナトリウム塩、アンモニウム塩、アンミン錯化合物等の各種化合物を使用することができ、イオン交換法、合浸法等の通常用いられる方法で担持することができる。通常のイオン交換法、合浸法による場合、金属原料は溶液で用いることが多く、その溶液には、酸あるいは塩基を添加して適当にpHを調節することにより好ましい結果を与える場合もあるが、本発明は担持法によって制限されるものではない。

【0018】本発明に用いられる触媒は多層化するため、ハニカム形状で使用する必要がある。この場合、ハニカム状の担体に本発明になるゼオライト系触媒を塗布して用いる。このハニカム材料としては、一般にコーゼライト質のものが広く用いられているが、これに限定されるものではなく、金属材料からなるハニカム担体も有効である。触媒の形状をハニカム状とすることにより、触媒と排気ガスとの接触面積が大きくなり、圧力損失も抑えられるため、振動があり、かつ限られた空間内で多量の排気ガスを処理することが要求される自動車の排気ガス浄化用触媒として用いる場合に有利となる。

【0019】本発明では、上記ハニカム状モノリス触媒を、空燃比が14.7以上のリーン条件で運転される内燃機関の排気系に設置し、酸素濃度が5%以上で、かつ窒素酸化物と炭化水素が反応して窒素酸化物を窒素に転化するのに必要な炭化水素量と窒素酸化物量の比率(=HC/NO<sub>x</sub>比)が10以下の排気ガスを流通、接触させることにより高効率の排気ガス浄化を実現する。酸素濃度が低く、炭化水素量が多すぎると、触媒表面上へのコーキングが起こりやすく、触媒劣化が促進されるので、上記排気ガス条件の範囲で使用するにより長時間の使用にも十分に耐えられ、高い浄化性能を維持できるのである。

【0020】

【実施例】以下、本発明を実施例によってさらに詳述するが、本発明はこれによって限定されるものではない。

【0021】<実施例1>

(1) 第1触媒層の形成

ジニトロジアンミン白金水溶液の中に活性アルミナの粉末を添加して良く攪拌した後、乾燥器中120℃で8時間乾燥、空気気流中500℃で2時間焼成し、Ptが約1.0wt%担持されたPt-活性アルミナ粉を得た。この触媒粉末に硝酸酸性アルミナゾル及び水とを磁性ボールミルポットに入れ、約20分間混合・粉砕してPt-活性アルミナのスラリーを得た。アルミナゾルの添加量は5wt%とした。このようにして得られたスラリーを、1平方インチ断面当たり約400個の流路を持つコーゼライト質ハニカム担体1.0Lに塗布し、150℃で熱風乾燥した後、500℃で1時間焼成して触媒コート量約30g/Lのハニカム触媒を得た。該ハニカム触媒を酢酸カルシウム、酢酸バリウム及び硝酸ランタンを含む混合水溶液に浸した後、120℃で乾燥し、500℃で1時間焼成して、Ca、Ba及びLaをハニカム触媒当たりそれぞれ0.1モル、0.2モル及び0.1モル含有した第1触媒層をコートしたハニカム触媒A1を得た。

【0022】(2) 第2触媒層の形成

SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>モル比が約35のH型βゼオライトの粉末に平均粒径が1.2nmのシリカゾル及び水とを加え、磁性ボールミルポットに入れて約30分間混合・粉砕しβゼオライト及びシリカを含むスラリーを得た。この時のシリカゾルの添加量はSiO<sub>2</sub>として25wt%とした。このように得られたスラリーを、上記実施例1で得られたハニカム触媒A1に塗布し、150℃の熱風乾燥に続き、500℃で1時間焼成してコート量を約60g/Lの第2触媒層を有するハニカム触媒体A2を得た。

【0023】上記スラリーを150℃乾燥後、500℃で1時間焼成して得た固形物を砕き、この細孔分布、細孔容積を測定した。この結果、直径1nm以上4nm以下の細孔の容積和は、直径1nm以上100nm以下の細孔の容積総和の68%であった。

【0024】(3) 第3触媒層の形成、3層触媒の調製  
濃度0.17Mの硝酸銅及び硝酸コバルト混合水溶液(Cu:Co=8:2)の中にSiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>モル比が約35のNa型MFIゼオライトの粉末を添加して良く攪拌し、次いで濾過することにより固液を分離した。上記の攪拌・濾過操作を3回繰り返すことにより、Cu及びCoをイオン交換担持したMFIゼオライト触媒ケーキを得た。このケーキを乾燥器中、120℃で24時間以上乾燥し、次いで電気炉を用い、大気雰囲気下600℃で4時間焼成することにより、Cuが3.9wt%、Coが0.8wt%担持されたCu-Co-MFI



触媒粉を得た。この触媒粉をアルミナゾル及び水と混合し、磁性ボールミルポットで20分間粉碎してスラリーとした。このスラリーを上記ハニカム触媒A2にコーティングし、乾燥器中120℃で8時間乾燥、空気気流中450℃で1時間焼成することにより、実施例1になる3層触媒1を得た。該第3触媒層のコート量は約220g/Lであった。

【0025】<実施例2>実施例1において、第3触媒層のMFIゼオライト粉末を $\text{SiO}_2/\text{Al}_2\text{O}_3$ モル比が約42のNa型βゼオライトに代えた以外は同様にして実施例2になる3層触媒2を得た。

【0026】<実施例3>実施例1において、第1触媒層のPt(1.0wt%)をPd-Rh(1.2wt%-0.2wt%)に代えた以外は同様にして実施例3になる3層触媒3を得た。

【0027】<実施例4>実施例1において、第1触媒層のCaO.1モル、BaO.2モル及びLaO.1モルを、MgO.05モル、BaO.13モル、K0.02モルに代えた以外は同様にして実施例4になる3層触媒4を得た。

【0028】<実施例5>実施例1において、第1触媒層のCaO.1モル、BaO.2モル及びLaO.1モルを、BaO.2モル、SrO.05モル、CsO.04、CeO.29モルに代えた以外は同様にして実施例5になる3層触媒5を得た。

【0029】<実施例6>実施例1において、第1触媒層のCaO.1モル、BaO.2モル及びLaO.1モルを、LaO.08モルに代えた以外は同様にして実施例6になる3層触媒6を得た。

【0030】<実施例7>実施例1において、1触媒層のCaO.1モル、BaO.02モル及びLaO.1モルを、BaO.3モル及びCeO.35モルに代えた以外は同様にして実施例7になる3層触媒7を得た。

【0031】<実施例8>実施例1において、実施例1における第2触媒層の調製において、シリカゾルの添加量を $\text{SiO}_2$ として12wt%とした以外は同様にして実施例8になる3層触媒8を得た。実施例1と同様にして第2触媒層用のスラリーを乾燥後、焼成して得た固形物を砕き、この細孔分布、細孔容積を測定した結果、直径1nm以上4nm以下の細孔の容積和は、直径1nm以上100nm以下の細孔の容積総和の54%であった。

【0032】<実施例9>実施例1における第2触媒層の調製において、シリカゾルの添加量を $\text{SiO}_2$ として46wt%とした以外は同様にして実施例9になる3層触媒9を得た。実施例1と同様にして第2触媒層用のスラリーを乾燥後、焼成して得た固形物を砕き、この細孔分布、細孔容積を測定した結果、直径1nm以上4nm以下の細孔の容積和は、直径1nm以上100nm以下の細孔の容積総和の50%であった。

【0033】<実施例10>実施例1における第2触媒層の調製において、シリカゾルの添加量を $\text{SiO}_2$ として60wt%とした以外は同様にして実施例10になる3層触媒10を得た。実施例1と同様にして第2触媒層用のスラリーを乾燥後、焼成して得た固形物を砕き、この細孔分布、細孔容積を測定した結果、直径1nm以上4nm以下の細孔の容積和は、直径1nm以上100nm以下の細孔の容積総和の45%であった。

【0034】<実施例11>実施例1における第2触媒層の調製において、シリカゾルの添加量を $\text{SiO}_2$ として6wt%とした以外は同様にして実施例11になる3層触媒11を得た。実施例1と同様にして第2触媒層用のスラリーを乾燥後、焼成して得た固形物を砕き、この細孔分布、細孔容積を測定した結果、直径1nm以上4nm以下の細孔の容積和は、直径1nm以上100nm以下の細孔の容積総和の40%であった。

【0035】<比較例1>実施例1において、第2触媒層を設けずに第1触媒層の上に直接第3触媒層をコーティングした以外は同様にして比較例1になる2層触媒Ref1を得た。

【0036】<比較例2>実施例1において、第2触媒層形成に際し、シリカゾルの代わりにアルミナゾルとし、その添加量をβゼオライトに対して $\text{Al}_2\text{O}_3$ として6wt%とした以外は同様にして比較例2になる3層触媒Ref2を得た。

【0037】<触媒性能試験例1>触媒の耐久処理；上記実施例及び比較例になる触媒を4気筒2.5Lディーゼルエンジンを設置したエンジンダイナモ装置の排気系に組み込み、触媒入口温度で600℃×50時間の急速耐久処理を行った。次に、4気筒2.5Lディーゼルエンジンを設置したエンジンダイナモ装置の排気系に、耐久処理を行った後の実施例及び比較例になる触媒を組み込み、触媒入口温度200℃～450℃の昇温時の $\text{NO}_x$ 転化性能を測定した。触媒入口温度の昇温速度は、約60℃/minであり、この時の排気ガス中の平均HC/ $\text{NO}_x$ 比は2.5、ガス空間速度は約4300h<sup>-1</sup>である。本装置では、エンジンマニホールドと触媒の間に設けたノズルから軽油を注入することにより排気ガス中のHC/ $\text{NO}_x$ 比を変化させることが可能である。図1に、触媒性能試験例1による実施例及び比較例の触媒の触媒入口温度400℃における $\text{NO}_x$ 浄化率を示す。実施例になる触媒では明らかに $\text{NO}_x$ 浄化率が高く、低温域でHC類を効率良くトラップし、かつ昇温過程でHCを高効率で利用しているために優れた $\text{NO}_x$ 浄化効率を示すと考えられる。また、第2層の細孔容積の比率、アルカリ、アルカリ土類及び希土類の担持量が本発明の請求項2、及び7の範囲を外れると、 $\text{NO}_x$ 低減率向上効果が低くなることが分かる。

【0038】<触媒性能試験例2>触媒性能試験例1の浄化性能テストにおいて、実施例2の触媒を用い、エン

ジン排気ガス中のHC濃度を変えることによりHC/NO<sub>x</sub>比を2.0から15.0の範囲で数水準かえてライトオフ・ライトオンの繰り返しを10回行った後のHC/NO<sub>x</sub>比に対する平均NO<sub>x</sub>浄化率(触媒入口温度400℃)を求めた。図2には、横軸HC/NO<sub>x</sub>比に対し、縦軸NO<sub>x</sub>の平均浄化率を示す。本発明になる触媒ではHC/NO<sub>x</sub>比が10以上の条件ではNO<sub>x</sub>浄化率の低下が顕著であり、むしろ適度なHC量で十分高い浄化率が得られることが分かる。

【0039】<触媒性能試験3>触媒性能試験例1の浄化性能テストにおいて、実施例2の触媒を用い、エンジン排気ガス組成の酸素濃度を2%から10%の範囲で数水準かえてライトオフ・ライトオンの繰り返しを10回行った後のライトオフ・ライトオンテストでのNO<sub>x</sub>成分について同様に平均NO<sub>x</sub>浄化率(触媒入口温度400℃)を求めた。図3には、横軸酸素濃度に対し、縦軸NO<sub>x</sub>の平均浄化率を示す。酸素濃度が5%以下でライトオフ・ライトオンテストを繰り返した場合、十分なNO<sub>x</sub>浄化率が得られないことが分かる。本触媒は5%以上のむしろ比較的酸素量の多い条件下で高性能を発揮する。

【0040】<第2触媒の細孔分布、細孔容積の測定>装置：島津製作所(マイクロメリテックス)製アサップ2400形

測定方法：N<sub>2</sub>ガス吸着による走容法

細孔分布データ解析：BJH法

サンプルの前処理方法：250℃で約15hの脱気処理(10<sup>-3</sup>torr以下)

解析データ：吸着側のデータから、メソ細孔直径に対して積算吸着細孔容積をプロットし、これから直径1nm以上4nm以下の細孔の容積和V<sub>4</sub>と、直径1nm以上100nm以下の細孔の容積和V<sub>100</sub>を求め、(V<sub>4</sub>/V<sub>100</sub>)×100(%)を算出した。

【0041】

【発明の効果】以上のように、本発明になる排気ガス浄化用触媒及び排気ガス浄化方法を用いると、150℃以下の低温を含む条件で、しかも低いHC/NO<sub>x</sub>比条件の排気ガスが高効率で浄化可能となるため、環境汚染が少なく、経済性(燃費)に優れた自動車を提供することができる。

【図面の簡単な説明】

【図1】本発明の実施例及び比較例になる触媒の排気ガスNO<sub>x</sub>浄化性能を示す図である。

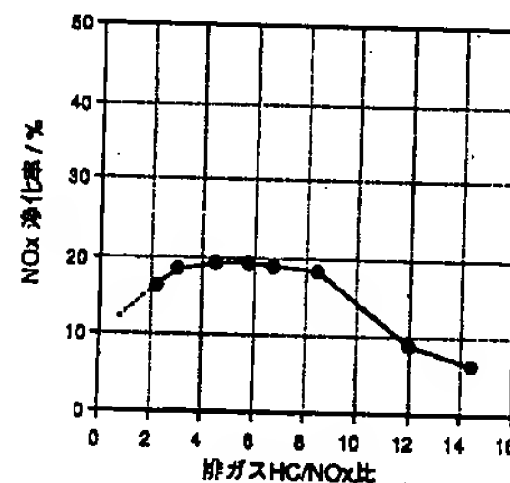
【図2】NO<sub>x</sub>浄化率に対する排気ガスHC/NO<sub>x</sub>比の影響を示す図である。

【図3】NO<sub>x</sub>浄化率に対する排気ガスO<sub>2</sub>濃度の影響を示す図である。

【図1】

触 媒	第2触媒層の細孔容積百分率 [V <sub>4</sub> /V <sub>100</sub> ]×100(%)	触媒入口400℃ NO <sub>x</sub> 浄化率(%)
実施例1	68	17.9
実施例2	68	18.3
実施例3	68	16.6
実施例4	68	17.4
実施例5	68	15.8
実施例6	68	15.1
実施例7	68	14.9
実施例8	54	17.8
実施例9	50	16.7
実施例10	45	14.8
実施例11	40	14.4
比較例1	—	12.5
比較例2	35	13.9

【図2】

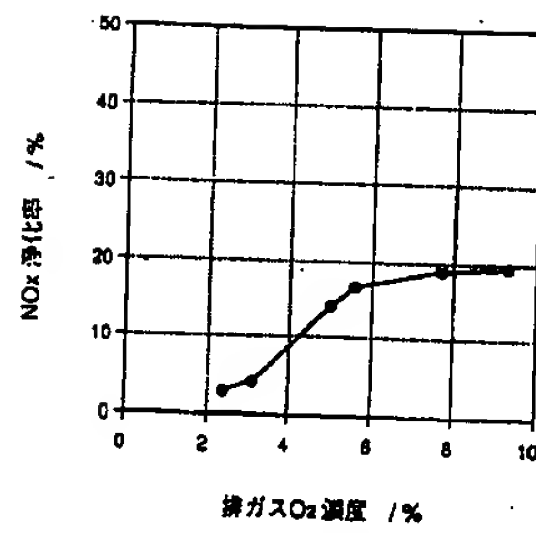




(7)

特開平11-253758

【図3】



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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the suitable catalyst for exhaust air gas cleanups for it to be efficient and purify the nitrogen oxide (NO<sub>x</sub>) in the RIN exhaust gas which contains charge, especially oxygen in the technology for purifying the exhaust gas discharged from an internal combustion engine, a combustor, etc. superfluously, and the exhaust air gas cleanup method

[0002]

[Description of the Prior Art] As a catalyst for purifying the included exhaust gas with which \*\*\*\* etc. spreads an oxidization component and a reduction component like the exhaust gas of the conventional automobile engine, the catalyst of 3 yuan is used widely. This is a catalyst which makes a principal component the activated alumina which supported various components including a noble-metals component and the Seria (Ce) components, such as Pt, Pd, and Rh, is efficient and can purify the hydrocarbon (HC), carbon monoxide (CO), and nitrogen oxide which are an injurious ingredient in exhaust gas.

[0003] On the other hand, the lean burn engine operated also with an air-fuel ratio higher than theoretical air fuel ratio from a viewpoint of the improvement in mpg and discharge curtailment of a carbon dioxide attracts attention in recent years. Conventionally which is operated near the theoretical air fuel ratio, as compared with the exhaust gas (it is called SUTOIKI exhaust gas) of an engine, the exhaust gas (it is called RIN exhaust gas) of such an engine has high oxygen content, and it becomes inadequate [ the above-mentioned 3 yuan catalyst ] purifying [ of nitrogen oxide ] it. Then, a new catalyst which is efficient and can purify the nitrogen oxide of lean burn engine exhaust gas was desired.

[0004] It sets in RIN exhaust gas and the zeolitic catalyst which supported various kinds of metal components to zeolites, such as Y type, an L type, a mordenite, and a MFI zeolite, is NO<sub>x</sub> under coexistence of hydrocarbons. It has the capacity which can be purified comparatively efficiently. Although it is admitted as this metal component of transition-metals components, such as copper (Cu), cobalt (Co), silver (Ag), nickel (nickel), and iron (Fe), and the noble-metals component that platinum (Pt) is effective NO<sub>x</sub> Cu-zeolitic catalyst which supported inside or Cu excelled [ NO<sub>x</sub> ] also in the bottom of the high rate-of-flow gas conditions comparatively. In order to show the decontamination-capacity force, expectation was hung on application to exhaust air gas cleanups, such as small mobile emission sources like an automobile, and a fixed type engine for private power generation.

[0005] However, since there is the following trouble in the zeolitic catalyst which supported the above-mentioned metal component, it has not resulted in utilization as a catalyst for exhaust air gas cleanups of the automobile driven on RIN conditions. First, NO<sub>x</sub> The temperature requirement which can be purified comparatively efficiently is narrow, and it is 150 to 300 degrees C NO<sub>x</sub> comparatively sufficient in a low temperature field especially. The decontamination-capacity force is not acquired. Moreover, there is comparatively little hydrocarbon in exhaust gas, especially it is HC/NO<sub>x</sub>. At the conditions from which a ratio becomes five to six or less, it is NO<sub>x</sub>. The decontamination-capacity force declines rapidly. Furthermore, since there is a fundamental trouble that degradation is very intense under the hot (600 degrees C or more) conditions (hydrothermal conditions) containing a steam, it has not resulted in utilization as a catalyst for exhaust air gas cleanups from a RIN barn automobile.

[0006] NO<sub>x</sub> in the above-mentioned degree field of low temperature To improvement in the decontamination-capacity force, for example by preparing a noble metal catalyst layer in the lower layer of Cu-zeolitic-catalyst layer, the heat of reaction in a noble metal catalyst layer is used, and operating the upper Cu-zeolitic catalyst from low temperature more is already proposed by JP,1-127044,A, JP,5-68888,A, etc. However, since degradation becomes intense in this case for the oxidation reaction heat in a lower layer noble metal catalyst layer or oxidization consumption of the HC is further carried out preferentially for the strong oxidization activity of a noble metal catalyst layer, it is NO<sub>x</sub>. Decline in the rate

of purification is caused. This influence is large especially when making a noble-metals component live together in Cu-zeolitic-catalyst layer (JP,1-31074,A, JP,5-168939,A).

[0007] moreover -- if Pt system catalyst is used -- 200-250 degrees C -- comparatively -- a low-temperature region -- NOx although it can convert -- N2 Not only inversion but generation of N2 O cannot be disregarded, but it is in the situation which cannot be used from the bad influence to environment if it remains as it is.

[0008] It is low HC/NOx at Cu-zeolitic catalyst, Pt system catalyst, and any catalyst. At the exhaust gas conditions of a ratio, it is NOx. Decontamination capacity becomes inadequate. Then, the purification method which supplies HC it is incomparable to a reducing agent, alcohols, etc. to a catalyst entrance in 2nd order is also proposed. In this case, although the method of mounting the tank of a reducing agent, the method of using fuel for a reducing agent directly, etc. are proposed, in the case of the former, the loading place of a tank, the trouble of the increase of a weight, and in the case of the latter, the trouble that the mpg of an engine falls victim arises.

[0009]

[Problem(s) to be Solved by the Invention] this invention is the degree field of low temperature, and low HC/NOx. At a ratio, it is NOx of a zeolitic catalyst. The decontamination-capacity force aims at offering the catalyst for the inadequate exhaust air gas cleanups of the practical use level which solved the above-mentioned trouble that degradation was intense under high-temperature-hot-water heat conditions, and raised the performance sharply, and the exhaust air gas cleanup method.

[0010]

[Means for Solving the Problem] One or more sorts of components as which this invention was chosen from Pt component, Pd component, and Rh component, The catalyst bed containing one or more sorts of components chosen from the alkali component, the alkaline-earth component, and the rare earth component is made into the 1st catalyst bed. The catalyst for exhaust air gas cleanups which prepared the 2nd catalyst bed which contains a silica and beta zeolite on it, and prepared further the 3rd catalyst bed which makes a principal component the zeolite containing Cu component and/or Co component on it is prepared. An A/F ratio installs this catalyst for exhaust air gas cleanups in the exhaust air system of the internal combustion engine operated on condition that 14.7 or more RIN. 5% or more of oxygen densities, and HC/NOx When 0 is exceeded, and a ratio circulates and contacts ten or less exhaust gas, a higher purification performance is attained by attaining the above-mentioned purpose and making the 2nd catalyst bed contain a silica and beta zeolite especially.

[0011] The catalyst which becomes this invention consists of the three above-mentioned layers, and has the big feature in the way of combining. The 1st catalyst bed is NOx. It oxidizes and is NOx with more high reactivity. It has the role converted into a seed and is NOx of the 3rd layer. The low-temperature activity of a reducing agent (reduction catalyst) is promoted. The 2nd catalyst bed carries out the trap of the HC efficiently, when exhaust gas is in the degree field of low temperature, and it is NOx of the 3rd layer. If it becomes the temperature region where reduction material operates HC will be supplied, and it is NOx. Reduction is promoted. Here, by making the 2nd catalyst bed contain a specific silica and specific beta zeolite, a convenient pore distribution is formed in the trap of HC, and purification efficiency is improved remarkably. The 1st and 2nd catalyst beds are NOx of the 3rd catalyst bed which deteriorated by \*\*\*\*\* (ing) under a high-temperature-hot-water heat condition. Oxidation capacity and HC adsorption are compensated and this compensates a deteriorated part of a catalyst.

[0012] How of the three above-mentioned layers to combine is NOx. The catalyst bed which contains a noble-metals component for the catalyst bed containing reduction material on the maximum front face is arranged in the lowest layer. NOx If a reduction material layer and a noble metal catalyst layer are contacted directly, it may not necessarily be desirable that the reaction of active ingredients occurs etc. in respect of catalyst de-activation. At this invention, it is NOx. By arranging a silica and beta zeolite between a reduction material layer and a noble metal catalyst layer, the adsorption property of HC was raised remarkably and high endurance which was excellent by this is also realized.

[0013] The influence of the mean particle diameter of the amount of silicas which the pore distribution in the 2nd catalyst bed is important, and it is made to contain in this invention, and its silica raw material is large. It is NOx when the capacity sum of with a 1nm or more diameter [ 4nm or less ] pore is 50% or more of capacity total of with a 1nm or more diameter [ 100nm or less ] pore as a pore distribution in the 2nd catalyst bed. The improvement effect of a purification performance is large. The amount of silicas made to contain has desirable 10 - 50 weight section to beta zeolite, and, as for the mean particle diameter of the silica raw material, it is desirable that it is [ 1nm or more ] 4nm or less. Here, one or more sorts of components chosen from Mg, calcium, K, Ba, La, Sr, Cs, and Ce as the alkali which the 1st catalyst bed contains, an alkaline earth, and a rare earth component are effective, and, as for the content of this component, an effect is demonstrated in 0.6 mols or less exceeding 0.1 mols of honeycomb-like monolithic catalyst 1L scaling. If many [ when there are few contents of this component, its effect is small, and / too ], the effect of noble

metals will be negated.

[0014] As for the silica / alumina ratio of beta zeolite of the 2nd catalyst bed used by this invention, it is desirable that it is [ or more 20 ] 150 or less. If a silica / alumina ratio is too small, a zeolite skeleton will become unstable, if a silica alumina ratio is too large conversely, the force of holding HC will become weak, and it becomes impossible to store HC to the temperature in which the 3rd catalyst bed carries out an operation start. Moreover, as an amount of beta zeolites of the 2nd catalyst bed, 100g or less is effective more than honeycomb-like monolithic catalyst 1L per 20g.

[0015] NO<sub>x</sub> As a zeolite of the 3rd catalyst bed containing reduction material, although Y type zeolite, a FERIE light, mordenite, etc. have activity, a MFI zeolite and/or beta zeolite are especially effective, and, as for its silica / alumina ratio, 80 or less [ 20 or more ] are desirable. If a silica / alumina ratio is too small, while a zeolite skeleton will become unstable, the amount of the active ingredient (Cu and/or Co) supported with the ion exchange becomes superfluous, dispersibility falls and the activity per active spot falls rapidly, pseudo-<sup>\*\*</sup> of the active spots tends to happen and degradation by the so-called sintering becomes easy to progress. However, if a silica / alumina ratio is too large, there will be too few active spots and sufficient activity will not be obtained.

[0016] Moreover, the amount of coats (support) of the 3rd catalyst bed has desirable 300g or less more than honeycomb-like monolithic catalyst 1L per 120g. If there are few amounts of coats of a catalyst bed, the activity under high simian virus will become inadequate, if many [ conversely / too ], diffusion of the reaction molecule to the 1st layer and the 2nd layer will be barred, or a bad influence, like pressure loss becomes large will arise. Since it will stabilize more and the high catalyst of thermal resistance and endurance will be acquired by hydrothermal processing, re-composition, etc. if crystallinity is raised, the zeolite in this invention is desirable.

[0017] In acquiring the catalyst for exhaust air gas cleanups which becomes this invention, as a raw material of the metal component supported to a zeolite, various compounds, such as an inorganic-acid salt, an oxide, organic acid chloride, a chloride, a carbonate, sodium salt, an ammonium salt, and an ammine complex compound, can be used, and it can support with methods usually used, such as an ion-exchange method and the <sup>\*\*\*\*</sup> method. Although a desirable result may be given by using a metal raw material in many cases with a solution, adding an acid or a base in the solution, and adjusting pH suitably when based on the usual ion-exchange method and the sinking-in method, this invention is not restricted by the supporting method.

[0018] In order to multilayer, it is necessary to use the catalyst used for this invention in a honeycomb configuration. In this case, the zeolitic catalyst which becomes this invention is applied and used for honeycomb-like support. As this honeycomb material, although the thing of the quality of a cordierite is generally used widely, the honeycomb support which is not limited to this and consists of a metallic material is also effective. Since the touch area of a catalyst and exhaust gas becomes large and pressure loss is also suppressed by making the configuration of a catalyst into the shape of a honeycomb, there is vibration, and it becomes advantageous when processing a lot of exhaust gas in the limited space uses as a catalyst for exhaust air gas cleanups of an automobile demanded.

[0019] In this invention, the above-mentioned honeycomb-like monolithic catalyst is installed in the exhaust air system of the internal combustion engine with which an air-fuel ratio is operated on 14.7 or more RIN conditions, an oxygen density is 5% or more, and when the ratio (= HC/NO<sub>x</sub> ratio) of the amount of hydrocarbons required for nitrogen oxide and a hydrocarbon to react and convert nitrogen oxide into nitrogen and the amount of nitrogen oxide circulates and contacts ten or less exhaust gas, an efficient exhaust air gas cleanup is realized. If an oxygen density is low and there are too many amounts of hydrocarbons, since coking to a catalyst front-face top will tend to happen and catalyst deactivation will be promoted, by using it in the range of the above-mentioned exhaust gas conditions, it can fully be equal also to prolonged use, and a high purification performance can be maintained.

[0020]

[Example] Hereafter, this invention is not limited by this although this invention is further explained in full detail according to an example.

[0021] the inside of the oven after adding the powder of an activated alumina and agitating in the formation dinitrodiammine platinum solution of the 1st catalyst bed of <an example 1 (1)> -- 120 degrees C -- the inside of 8-hour dryness and an air current -- 500 degrees C -- 2 hours -- calcinating -- Pt -- about 1.0 wt(s)% -- supported pt-activated-alumina powder was obtained A nitric-acid acid alumina sol and water were put into this catalyst powder at the magnetic pole mill pot, it mixed and ground for about 20 minutes, and the slurry of Pt-activated alumina was obtained. The addition of an alumina sol was made into 5wt(s)%. Thus, after it applied the obtained slurry to nature honeycomb support of cordierite 1.0L with about 400 passage per 1 square inch cross section and it carried out hot air drying at 150 degrees C, it calcinated at 500 degrees C for 1 hour, and the honeycomb catalyst of catalyst coat <sup>\*\*\*\*</sup> 30 g/L was obtained. After dipping this honeycomb catalyst in the mixed-water solution containing a calcium acetate, a barium acetate, and a lanthanum nitrate, it dried at 120 degrees C, it calcinated at 500 degrees C for 1 hour, and



- honeycomb-catalyst aluminum which carried out the coat of per [ of 0.1 mols of each ] honeycomb catalyst, 0.2 mols, and the 1st catalyst bed contained 0.1 mols for calcium, Ba, and La was obtained.
- [0022] (2) Formation SiO<sub>2</sub> / aluminum 2O<sub>3</sub> of the 2nd catalyst bed The slurry in which a mole ratio adds the silica sol and water whose mean particle diameter is 1.2nm to the powder of the H type beta zeolite of about 35, puts into a magnetic ball mill pot, mixes and grinds for about 30 minutes, and contains beta zeolite and a silica was obtained. The addition of the silica sol at this time is SiO<sub>2</sub>. It carried out and could be 25wt(s)%. Thus, the obtained slurry was applied to honeycomb-catalyst aluminum obtained in the above-mentioned example 1, and the honeycomb-catalyst object A2 which calcinates at 500 degrees C for 1 hour, and has the 2nd catalyst bed of about 60 g/L for the amount of coats was acquired following 150-degree C hot air drying.
- [0023] The solid which calcinated the above-mentioned slurry for 1 hour, and obtained it at 500 degrees C after 150-degree-C dryness was broken, and this pore distribution and pore volume were measured. Consequently, the capacity sum of with a 1nm or more diameter [ 4nm or less ] pore was 68% of capacity total of with a 1nm or more diameter [ 100nm or less ] pore.
- [0024] (3) They are SiO<sub>2</sub> / aluminum 2O<sub>3</sub> in the copper nitrate of manufacture concentration 0.17M of formation of the 3rd catalyst bed, and a three-layer catalyst, and a cobalt-nitrate mixed-water solution (Cu:Co=8:2). The mole ratio could add the powder of the Na type MFI zeolite of about 35, and it agitated, and separated solid-liquid by subsequently filtering. the above-mentioned churning / filtration operation -- 3 circuit \*\*\*\*\* -- by things, the MFI zeolite-catalyst cake which carried out ion-exchange support of Cu and the Co was obtained drying this cake at 120 degrees C among an oven for 24 hours or more, and calcinating at 600 degrees C under air atmosphere for 4 hours using an electric furnace subsequently -- Cu -- 3.9w% and Co -- 0.8wt(s)% -- the supported Cu-Co-MFI catalyst powder was obtained This catalyst powder was mixed with an alumina sol and water, the magnetic ball mill pot ground for 20 minutes, and it considered as the slurry. The three-layer catalyst 1 which becomes an example 1 was acquired by coating the above-mentioned honeycomb catalyst A2 with this slurry, and calcinating at 450 degrees C among 8-hour dryness and an air air current by 120 degrees C among an oven for 1 hour. The amount of coats of this 3rd catalyst bed was about 220 g/L.
- [0025] It sets in the <example 2> example 1, and they are SiO<sub>2</sub> / aluminum 2O<sub>3</sub> about the MFI zeolite powder of the 3rd catalyst bed. Except that the mole ratio replaced with the Na type beta zeolite of about 42, the three-layer catalyst 2 which becomes an example 2 similarly was acquired.
- [0026] In the <example 3> example 1, the three-layer catalyst 3 which becomes an example 3 similarly was acquired except having replaced Pt (1.0wt%) of the 1st catalyst bed with Pd-Rh (1.2wt%-0.2wt%).
- [0027] In the <example 4> example 1, the three-layer catalyst 4 which becomes an example 4 similarly was acquired except having replaced 0.1 mols of calcium of the 1st catalyst bed, 0.2 mol of Ba(s), and 0.1 mol of La(s) with 0.05 mo [ of Mg ], and 0.13 mol [ of Ba(s) ] K 0.02 mols.
- [0028] In the <example 5> example 1, the three-layer catalyst 5 which becomes an example 5 similarly was acquired except having replaced 0.1 mols of calcium of the 1st catalyst bed, 0.2 mol of Ba(s), and 0.1 mol of La(s) with 0.2 mol of Ba(s), 0.05 mols of Sr, Cs 0.04, and 0.29 mol of Ce(s).
- [0029] In the <example 6> example 1, the three-layer catalyst 6 which becomes an example 6 similarly was acquired except having replaced 0.1 mols of calcium of the 1st catalyst bed, 0.2 mol of Ba(s), and 0.1 mol of La(s) with 0.08 mo of La(s).
- [0030] In the <example 7> example 1, the three-layer catalyst 7 which becomes an example 7 similarly was acquired except having replaced 0.1 mols of calcium of one catalyst bed, 0.02 mol of Ba(s), and 0.1 mol of La(s) with 0.3 mol of Ba(s), and 0.35 mol of Ce(s).
- [0031] In the <example 8> example 1, it sets to manufacture of the 2nd catalyst bed in an example 1, and is the addition of a silica sol SiO<sub>2</sub> The three-layer catalyst 8 which becomes an example 8 similarly was acquired except having carried out and having considered as 12wt(s)%. As a result of breaking the solid calcinated and obtained and measuring this pore distribution and pore volume after drying the slurry for the 2nd catalyst bed like an example 1, the capacity sum of with a 1nm or more diameter [ 4nm or less ] pore was 54% of capacity total of with a 1nm or more diameter [ 100nm or less ] pore.
- [0032] In manufacture of the 2nd catalyst bed in the <example 9> example 1, the three-layer catalyst 9 which becomes an example 9 similarly was acquired except having considered as 46wt(s)%, having used the addition of a silica sol as SiO<sub>2</sub>. As a result of breaking the solid calcinated and obtained and measuring this pore distribution and pore volume after drying the slurry for the 2nd catalyst bed like an example 1, the capacity sum of with a 1nm or more diameter [ 4nm or less ] pore was 50% of capacity total of with a 1nm or more diameter [ 100nm or less ] pore.
- [0033] In manufacture of the 2nd catalyst bed in the <example 10> example 1, the three-layer catalyst 10 which

becomes an example 10 similarly was acquired except having considered as 60wt(s)%, having used the addition of a silica sol as SiO<sub>2</sub>. As a result of breaking the solid calcinated and obtained and measuring this pore distribution and pore volume after drying the slurry for the 2nd catalyst bed like an example 1, the capacity sum of with a 1nm or more diameter [ 4nm or less ] pore was 45% of capacity total of with a 1nm or more diameter [ 100nm or less ] pore.

[0034] In manufacture of the 2nd catalyst bed in the <example 11> example 1, the three-layer catalyst 11 which becomes an example 11 similarly was acquired except having considered as 6wt(s)%, having used the addition of a silica sol as SiO<sub>2</sub>. As a result of breaking the solid calcinated and obtained and measuring this pore distribution and pore volume after drying the slurry for the 2nd catalyst bed like an example 1, the capacity sum of with a 1nm or more diameter [ 4nm or less ] pore was 40% of capacity total of with a 1nm or more diameter [ 100nm or less ] pore.

[0035] In the <example 1 of comparison> example 1, the two-layer catalyst Ref1 which becomes the example 1 of comparison similarly was acquired except having coated the 3rd catalyst bed directly on the 1st catalyst bed, without preparing the 2nd catalyst bed.

[0036] In the <example 2 of comparison> example 1, it considers as an alumina sol instead of a silica sol on the occasion of the 2nd catalyst bed formation, and is aluminum 2O<sub>3</sub> to beta zeolite about the addition. The three-layer catalyst Ref2 which becomes the example 2 of comparison similarly was acquired except having carried out and having considered as 6wt(s)%.

[0037] Durable processing of the <example 1 of catalyst performance test> catalyst; the catalyst which becomes the above-mentioned example and an example of comparison was included in the exhaust air system of engine DYNAMO equipment which installed the 4-cylinder 2.5L DIZE engine, and rapid durable processing of 600 degree-Cx 50 hours was performed with catalyst inlet temperature. Next, the catalyst which becomes an example and the example of comparison after performing durable processing in the exhaust air system of engine DYNAMO equipment which installed the 4-cylinder 2.5L diesel power plant is incorporated, and it is NO<sub>x</sub> at the time of a temperature up with a catalyst inlet temperature of 200 degrees C - 450 degrees C. The inversion performance was measured. The programming rate of catalyst inlet temperature is about 60 degrees C/min, and is average HC/NO<sub>x</sub> in the exhaust gas at this time. As for SU space velocity, 2.5\*\* of a ratio is abbreviation 43000h<sup>-1</sup>. It is HC/NO<sub>x</sub> in exhaust gas by pouring in gas oil from the nozzle prepared between the engine manifold and the catalyst with this equipment. It is possible to change a ratio. NO<sub>x</sub> in the catalyst inlet temperature of 400 degrees C of the catalyst of the example according to the example 1 of a catalyst performance test to drawing 1, and the example of comparison The rate of purification is shown. At the catalyst which becomes an example, it is NO<sub>x</sub> clearly. The rate of purification is high, and the trap of the HC is carried out efficiently in a low-temperature region, and it is thought that the NO<sub>x</sub> purification efficiency in which it excelled since it was efficient and HC was used in temperature up process is shown. Moreover, it is NO<sub>x</sub> if the amount of support of the ratio of the pore volume of the 2nd layer, alkali, an alkaline earth, and rare earth separates from the range of the claims 2 and 7 of this invention. The improvement effect in the rate of reduction is low, and a bird clapper is known.

[0038] It is HC/NO<sub>x</sub> by changing HC concentration in engine exhaust gas using the catalyst of an example 2 in the purification performance test of the example 1 of the <example 2 of catalyst performance test> catalyst performance test. HC/NO<sub>x</sub> after obtaining a ratio in a number level in 2.0 to 15.0 and performing the repeat of light-off-Right On 10 times Average NO<sub>x</sub> to a ratio It asked for the rate of purification (catalyst inlet temperature of 400 degrees C). In drawing 2, it is horizontal-axis HC/NO<sub>x</sub>. It is a vertical axis NO<sub>x</sub> to a ratio. The rate of average purification is shown. At the catalyst which becomes this invention, it is HC/NO<sub>x</sub>. A ratio is NO<sub>x</sub> at ten or more conditions. Decline in the rate of purification is remarkable, and it turns out that the sufficiently high rate of purification is rather obtained in the moderate amount of HC.

[0039] NO<sub>x</sub> in the light-off-Right On test after obtaining the oxygen density of engine exhaust gas composition in a number level in 2 to 10% of range and performing the repeat of light-off-Right On 10 times using the catalyst of an example 2 in the purification performance test of the example 1 of the <catalyst performance test 3> catalyst performance test It is Average NO<sub>x</sub> similarly about a component. It asked for the rate of purification (catalyst inlet temperature of 400 degrees C). It is [ as opposed to / a horizontal-axis oxygen density / in drawing 3 ] a vertical axis NO<sub>x</sub>. The rate of average purification is shown. It is sufficient NO<sub>x</sub> when an oxygen density repeats a light-off-Right On test at 5% or less. It turns out that the rate of purification is not obtained. This catalyst demonstrates high performance under 5% or more of conditions with rather comparatively many amounts of oxygen.

[0040] The pretreatment method of the \*\*\*\* method pore distribution data analysis;BJH method sample by <measurement of pore distribution [ of the 2nd catalyst ], and pore volume> equipment; Shimadzu (Micromeritics) ASAPPU 2400 type measuring method;N<sub>2</sub> gas adsorption; it is about 15h deaeration processing (10 to 3 or less torrs) at 250 degrees C.

Analysis data; addition adsorption pore volume is plotted from the data by the side of adsorption to a meso pore diameter, and it is the capacity sum V4 of with a 1nm or more diameter [ 4nm or less ] pore after this. Capacity total V100 of with a 1nm or more diameter [ 100nm or less ] pore It asked and  $x(V4 / V100)100(\%)$  was computed.

[0041]

[Effect of the Invention] As mentioned above, when the catalyst for exhaust air gas cleanups and the exhaust air gas cleanup method of becoming this invention are used, it is conditions including low temperature 150 degrees C or less, and, moreover, is low HC/NOx. Since purification of the exhaust gas of ratio conditions is attained [ that it is efficient and ], there is little environmental pollution and it can offer the automobile excellent in economical efficiency (mpg).

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[Translation done.]



**\* NOTICES \***

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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**CLAIMS**

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**[Claim(s)]**

- [Claim 1] One or more sorts of components chosen from the platinum (Pt) component, the palladium (Pd) component, and the rhodium (Rh) component. The 3rd catalyst bed which makes the catalyst bed containing one or more sorts of components chosen from the alkali component, the alkaline-earth component, and the rare earth component the 1st catalyst bed, and makes a principal component the zeolite which prepares the 2nd catalyst bed containing beta zeolite on it, and contains a copper (Cu) component and/or a cobalt (Co) component on it further. It is the catalyst for exhaust air gas cleanups equipped with the above, and is characterized by making the 2nd catalyst bed contain a silica (SiO<sub>2</sub>).
- [Claim 2] The catalyst for exhaust air gas cleanups characterized by the capacity sum of with a 1nm or more diameter [ of the 2nd catalyst bed / 4nm or less ] pore being 50% or more of capacity total of with a 1nm or more diameter [ 100nm or less ] pore in the catalyst for exhaust air gas cleanups according to claim 1.
- [Claim 3] The catalyst for exhaust air gas cleanups to which the amount of silicas contained in the 2nd catalyst bed is characterized by being 10 - 50 weight section to beta zeolite in the catalyst for exhaust air gas cleanups according to claim 1 or 2.
- [Claim 4] The catalyst for exhaust air gas cleanups characterized by for a claim 1 or 3 not being but the silica of the 2nd catalyst bed using as a raw material the silica sol which is 1nm or more particle size of 4nm or less in the catalyst for exhaust air gas cleanups given in that term.
- [Claim 5] The catalyst for exhaust air gas cleanups characterized by the alkali, alkaline earths, and rare earth components which a claim 1 or 4 is not but the 1st catalyst bed contains in the catalyst for exhaust air gas cleanups of a publication in that term being one or more sorts of components chosen from magnesium (Mg), calcium (calcium), a potassium (K), barium (Ba), a lanthanum (La), strontium (Sr), caesium (Cs), and the cerium (Ce).
- [Claim 6] the content of one or more sorts of components chosen from the alkali, alkaline earth, and rare earth component which a claim 1 or 5 is not but the 1st catalyst bed contains in the catalyst for exhaust air gas cleanups of a publication in that term -- per [ honeycomb-like monolithic catalyst 1L ] -- the catalyst for exhaust air gas cleanups characterized by containing in 0.6 mols or less exceeding 0.1 mols
- [Claim 7] It is the exhaust air gas cleanup method using the catalyst for exhaust air gas cleanups given in a claim 1 or one term of 6. The aforementioned catalyst for exhaust air gas cleanups is installed in the exhaust air system of the internal combustion engine with which an air-fuel ratio (Air/Fuel ratio = A/F) is operated on 14.7 or more RIN conditions. an oxygen density at 5% or more And the exhaust air gas cleanup method characterized by for the ratio (a following and HC/NO<sub>x</sub> ratio and brief sketch) of the amount of hydrocarbons required for nitrogen oxide and a hydrocarbon to react and convert nitrogen oxide into nitrogen and the amount of nitrogen oxide exceeding 0, and circulating and contacting ten or less exhaust gas.

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[Translation done.]